

## **Indicator: Atmospheric Deposition of Mercury (038)**

Mercury is found naturally in the environment and is also emitted into the air from industrial processes, like coal combustion and waste incineration (see “Mercury Emissions” indicator). Wet atmospheric deposition of mercury (mercury that falls to the Earth’s surface in the form of rain or snow) is an important environmental issue, particularly in aquatic settings. When mercury enters water bodies, whether from direct deposition or runoff, microorganisms can convert mercury into methylmercury, a highly toxic chemical (Wiener et al., 2002). The rate of this chemical conversion depends on environmental conditions such as the pH of a water body. For example, lakes heavily influenced by acid deposition often form more methylmercury than do similar lakes that are not acidified (Watras et al., 1994). Once formed in the water, small aquatic plants (phytoplankton) can absorb methylmercury. Methylmercury then enters small aquatic animals (zooplankton) that consume the plants. Through this process, the methylmercury continues to work its way up the food chain becoming more concentrated as it goes. For this reason, fish species higher in the food chain, such as sharks and swordfish, tend to have much higher methylmercury concentrations than fish species lower in the food chain.

Methylmercury in fish tissue presents a health risk to humans who eat fish from waters impacted by atmospheric deposition and other environmental releases (see the “Blood Mercury Level” indicator). Methylmercury also can have adverse behavioral and reproductive impacts on fish and both birds and mammals that eat significant amounts of fish (Wiener et al., 2002).

This indicator reflects the amount of mercury deposited to the United States in wet precipitation (rain or snow). The data were collected as part of the National Atmospheric Deposition Program (NADP) Mercury Deposition Network (MDN). The network began with 13 monitoring sites in 1995 and now has over 85 sites in operation. Most existing MDN sites are located in eastern North America from Minnesota to the Canadian Maritime Provinces and along the U.S. Atlantic and Gulf coasts. Precipitation samples are collected weekly and aggregated to provide annual average concentrations and annual wet deposition. MDN sites are located to measure broad geographical patterns of deposition that are not markedly influenced by local emissions. Annual wet deposition of mercury is calculated by multiplying concentrations in rainfall by the total precipitation amounts and summing them for the calendar year.

### **What the Data Show**

Figure 038-1 shows the average mercury concentrations in precipitation measured across several regions of the U.S. in 2003 using shaded contours. The dots and numbers on the map correspond to the annual average concentration at each MDN monitoring site. Regional estimates of concentrations in precipitation can be made for the eastern United States, but there are too few monitoring stations located in the western United States to make such estimates there. As the figure shows, the highest mercury concentrations in precipitation were observed in the south. Two southwestern monitoring stations where there is very little rainfall had average concentrations of 27.0 and 16.4 ng/L and at four stations in central and southern Florida had average concentrations 16.1-16.4 ng/L. High concentrations (16.7 ng/L) were also found at one monitoring site in southeastern Wisconsin. In general, concentrations in the Northeastern and Mid-Atlantic states tended to be lower than those in the Midwestern and Southeastern United States.

Figure 038-2 shows data for annual wet deposition of mercury across several regions of the U.S. in 2003 using shaded contours. Wet deposition is a better measure than concentration of the amount of mercury that goes into the environment through precipitation. The dots and numbers on the map correspond to the annual deposition amount at each MDN monitoring site. Regional estimates of deposition amount can be made for the eastern United States, but there are too few monitoring stations located in the western United States to make such estimates there. The highest levels of wet mercury deposition were found in the South along the Gulf coast and extending up to the Mid-Atlantic and the Ohio River Valley. Lower wet

deposition levels were observed in Minnesota, Wisconsin, New York, New England, and the Western sites.

### **Indicator Limitations**

- Although monitoring stations are placed in many areas impacted by major mercury sources, the spatial coverage provided by MDN is limited in the western and central United States.
- Data are not available to characterize dry deposition of mercury, or the amount of mercury that falls to the Earth during periods of no precipitation as gases or particles. Dry deposition is believed to make up a substantial portion of the total amount deposited through atmospheric deposition.
- The precise relationship between the total mercury measured at MDN sites and the amount of methylmercury in the environment is currently unknown.

### **Data Sources**

National Atmospheric Deposition Program (NADP): <http://nadp.sws.uiuc.edu/>. This site includes a link to the Mercury Deposition Network (MDN) website.

### **References**

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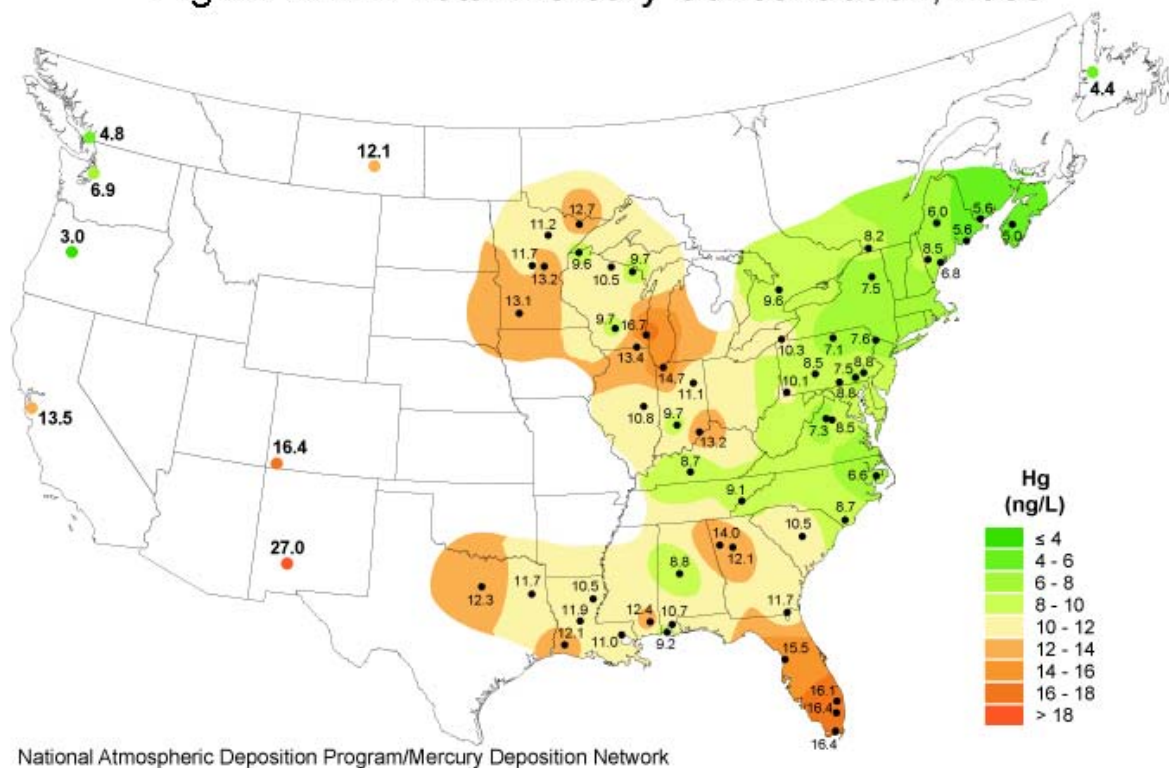
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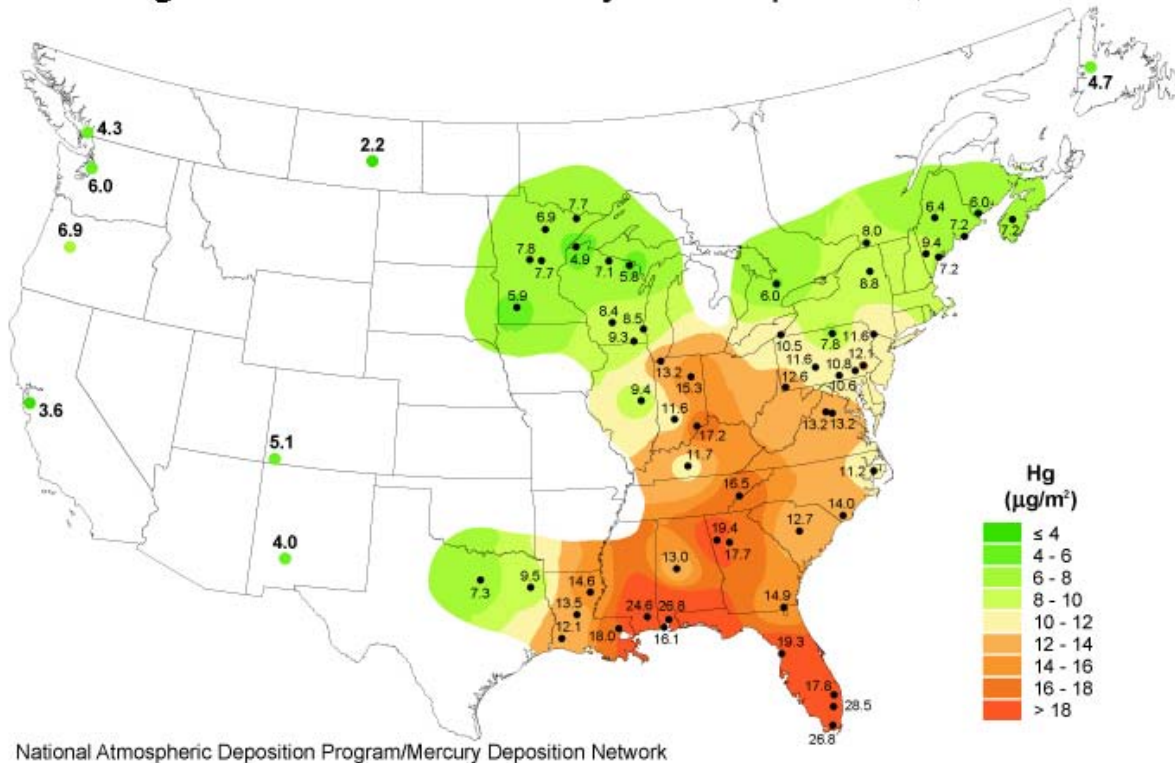
## Graphics

Figure 038-1: Total Mercury Concentration, 2003



National Atmospheric Deposition Program/Mercury Deposition Network

Figure 038-2: Total Mercury Wet Deposition, 2003



## R.O.E. Indicator QA/QC

**Data Set Name:** ATMOSPHERIC DEPOSITION OF MERCURY

**Indicator Number:** 038 (89136)

**Data Set Source:** NADP <http://nadp.sws.uiuc.edu/>

**Data Collection Date:** ongoing 1995-present

**Data Collection Frequency:** weekly

**Data Set Description:** Atmospheric Deposition of Mercury

**Primary ROE Question:** What are the trends in outdoor air quality and effects on human health and ecological systems?

## Question/Response

**T1Q1** Are the physical, chemical, or biological measurements upon which this indicator is based widely accepted as scientifically and technically valid?

Yes, MDN uses standardized methods for data collection and analyses based on similar scientifically and technically valid methods used for the long-term NADP National

Trends Network. Weekly precipitation samples are collected in a modified Aerochem Metrics model 301 collector. The "wet-side" sampling glassware is removed from the collector every Tuesday and mailed to the Hg Analytical Laboratory (HAL) at Frontier Geosciences in Seattle, WA for analysis by cold vapor atomic fluorescence. The methods and units of uncertainty of measurement are detailed in the MDN and NADP QA plan available at <http://nadp.sws.uiuc.edu/QA/>. Vermette, S., Lindberg, S., Bloom, N., 1995. Field tests for a regional mercury deposition network sampling design and preliminary test results. *Atmospheric Environment* 29, 1247-1251. Lindberg, S., Vermette, S., 1995. Workshop on sampling mercury in precipitation for the National Atmospheric Deposition Program. *Atmospheric Environment* 29, 1219-1220.

**T1Q2** Is the sampling design and/or monitoring plan used to collect the data over time and space based on sound scientific principles?

Yes, as documented in the NADP/MDN QA plan <http://nadp.sws.uiuc.edu/QA/>, the MDN monitoring program is designed to ensure samples are regionally representative and not unduly influenced by individual local sources. MDN recognizes that the representativeness of a given site location, or of the distribution of a group of sites, is best determined in the context of the planned application of the data. There are objectives for monitoring locations as well as for the samples collected for chemistry. These objectives are (1) to obtain and analyze individual samples which are qualitatively and quantitatively representative of the precipitation that fell (sample representativeness), and (2) to obtain network data that represent broad-scale geographical patterns in concentrations and deposition (spatial representativeness). The following journal articles and presentations describe the network design, including the sampling and analytical protocols, used in the MDN: Lindberg, S. and Vermette, S. 1995. Workshop on Sampling Mercury in Precipitation for the National Atmospheric Deposition Program. *Atmospheric Environment*. 29, 1219-1220. Vermette, S., Lindberg, S., and Bloom, N. 1995. Field Tests for a Regional Mercury Deposition Network - Sampling Design and Preliminary Test Results. *Atmospheric Environment*. 29, 1247-1251. Welker, M. and Vermette, S.J., 1996. Mercury Deposition Network: QA/QC Protocols. Paper 96-RP129.01, Proceedings of the 89th Annual Meeting of the Air and Waste Management Association, A&WMA, Pittsburgh, PA. Swain, E.B., Engstrom, D.R., Brigham, M.E., Henning, T.A., Brezonik, P.L., 1992. Increasing rates of atmospheric mercury deposition in midcontinental North America. *Science* 257, 784-787. Sweet, C.W. and Prestbo, E. 1999. Wet Deposition of Mercury in the U.S. and Canada. Presented at "Mercury in the Environment Specialty Conference", September 15-17, 1999, Minneapolis, MN. Proceedings published by Air and Waste Management Association, Pittsburgh, PA.

**T1Q3** Is the conceptual model used to transform these measurements into an indicator widely accepted as a scientifically sound representation of the phenomenon it indicates?

Yes, the methods used to calculate wet Hg deposition from NADP/MDN data are scientifically and technically valid. Wet deposition of mercury depends on both the concentration in rain and the total rainfall amount. Mercury wet deposition is calculated by multiplying rain gage precipitation amount (mm) by total mercury concentrations

(ng/L) reported by the central laboratory. MDN methods of determining wet deposition values have undergone extensive peer review. Assessments of changes in NADP methods are developed primarily through the academic and scientific community and reviewed through the technical literature process. For more information on sampling procedures and calculations, refer to the NADP/MDN Quality Assurance Plan <http://nadp.sws.uiuc.edu/QA/>. In addition, a number of researchers have estimated that direct wet deposition accounts for between 50-90% of the mercury entering surface waters. Sorensen, J.A., Glass, G.E., Schmidt, K.W., Huber, J.K., Rapp, G.R. 1990. Airborne mercury deposition and watershed characteristics in relation to mercury concentrations in water, sediments, plankton, and fish of eighty northern Minnesota lakes. *Environmental Science and Technology* 24, 1716-1727. Scherbatskoy, T., Burke, J.M., Rea, A.W., Keeler, G.J., 1997. Atmospheric mercury deposition and cycling in the Lake Champlain Basin of Vermont. In *Atmospheric Deposition of Contaminants to the Great Lakes and Coastal Waters*, J.E. Baker (Ed.), SETAC Press, Pensacola, FL, pp. 245-257. Lamborg, C.H., Fitzgerald, W.F., Vandal, G.M., Rolfhus, K.R., 1995. Atmospheric mercury in northern Wisconsin: sources and species. *Water, Air, & Soil Pollution* 80, 189-198. Mason, R.P., Lawson, N.M., Sullivan, K.A., 1997. Atmospheric deposition to the Chesapeake Bay – regional and local sources. *Atmospheric Environment* 31, 3531-3540. Landis, M.S., Keeler, G.J., 2002. Atmospheric mercury deposition to Lake Michigan during the Lake Michigan mass balance study. *Environmental Science and Technology* 36, 4518-4524. Mason, R.P., Lawson, N.M., Lawrence, A.L., Lee, J.G., Leaner, J.J., Sheu, G.R., 1999. Mercury in the Chesapeake Bay. *Marine Chemistry* 665, 114-119.

**T2Q1** To what extent is the indicator sampling design and monitoring plan appropriate for answering the relevant question in the ROE?

MDN is the nation's only long-term, consistent survey of mercury wet-deposition concentrations and fluxes to show regional and national patterns of mercury wet deposition. At the time of NADP's 2004 Scientific Symposium & Annual Technical Committee Meeting (September 21-24) there were eighty-four active MDN monitoring sites. Precipitation samples are collected weekly using standard procedures in a modified Aerochem Metrics model 301 collector to preserve mercury. The "wet-side" sampling glassware is removed from the collector every Tuesday and mailed to the Hg Analytical Laboratory (HAL) at Frontier Geosciences in Seattle, WA for analysis by cold vapor atomic fluorescence. The MDN provides data for total mercury, but also includes methylmercury if desired by a site sponsor. Data is most often aggregated to provide seasonal and annual averages.

**T2Q2** To what extent does the sampling design represent sensitive populations or ecosystems?

As documented in the MDN QA plan <http://nadp.sws.uiuc.edu/QA/>), MDN uses long established NADP local and regional siting criteria in an attempt to obtain samples that are regionally representative (i.e., represent major physiographic, agricultural, aquatic and forested areas within states, regions or Eco-regions). Data collected are intended to be indicative of broad geographical patterns of deposition and are not markedly



influenced by local emissions. Mercury deposition from the atmosphere is the primary pathway by which it enters sensitive aquatic systems where conversion to methyl mercury (MMHg) in fish can give rise to harmful human health and environmental impacts. The data is used to develop an information base on spatial and seasonal trends in mercury deposited to surface waters, forested watersheds, and other sensitive receptors. Regional criteria will be relaxed in some instances in order to research Hg deposition in biologically or ecologically important areas. Most of the current MDN sites are located in eastern North America from Minnesota to the Canadian Maritime Provinces and along the U.S. Atlantic and Gulf coasts. These regions generally have the most sensitive lakes and highest number of fish advisories.

**T2Q3** Are there established reference points, thresholds or ranges of values for this indicator that unambiguously reflect the state of the environment?

No, however, deposition levels are a valuable resource for determining Total Maximum Daily Load (TMDL) estimates. The MDN database will be particularly useful to evaluate the effectiveness of any state or federally mandated controls on mercury emissions.

**T3Q1** What documentation clearly and completely describes the underlying sampling and analytical procedures used?

The sampling and analytical procedures are documented in the MDN and NADP Quality Assurance plan. Quality assurance information is available on the web at <http://nadp.sws.uiuc.edu/QA>

**T3Q2** Is the complete data set accessible, including metadata, data-dictionaries and embedded definitions or are there confidentiality issues that may limit accessibility to the complete data set?

NADP/MDN Data are available via the web at <http://nadp.sws.uiuc.edu/mdn/> for the transition network (1995) and for 1996 through the second quarter of 2003.

**T3Q3** Are the descriptions of the study or survey design clear, complete and sufficient to enable the study or survey to be reproduced?

Yes, refer to the NADP and MDN QA plan for details on the monitoring plan and descriptions of the survey design

**T3Q4** To what extent are the procedures for quality assurance and quality control of the data documented and accessible?

Analysis of precipitation samples for total- and methylmercury is performed by Frontier Geosciences, Inc., Seattle WA, USA. Frontier Geosciences provides the environmental sciences community with uncompromisingly high-quality contract research, project design and management, and analytical chemistry services concerned with the sources, fate and effects of trace metals. The QA Plan for the laboratory can be downloaded at

<http://nadp.sws.uiuc.edu/QA/> The procedures for quality assurance and quality control are documented and accessible in the NADP and MDN QA plan at <http://nadp.sws.uiuc.edu/QA/>.

**T4Q1** Have appropriate statistical methods been used to generalize or portray data beyond the time or spatial locations where measurements were made (e.g., statistical survey inference, no generalization is possible)?

Yes, appropriate statistical methods have been used for spatial interpolation of wet deposition and calculating volume-weighted mercury concentration annual means. For more information, refer to the NADP/MDN Quality Assurance Plan available at <http://nadp.sws.uiuc.edu/QA/>.

**T4Q2** Are uncertainty measurements or estimates available for the indicator and/or the underlying data set?

Yes, the objectives and goals for data completeness, precision, bias, and comparability are addressed in the NADP/MDN QA plan at <http://nadp.sws.uiuc.edu/QA/>.

**T4Q3** Do the uncertainty and variability impact the conclusions that can be inferred from the data and the utility of the indicator?

The MDN network is designed to minimize sources of error or uncertainty in sample collection by utilizing uniform sampling equipment and following standardized operating procedures at all individual sites. Variability in site location and limited geographic coverage, particularly in the western United States do impact a broader national surveys of mercury deposition.

**T4Q4** Are there limitations, or gaps in the data that may mislead a user about fundamental trends in the indicator over space or time period for which data are available?

Sites are concentrated in the East in those States with and there is limited geographic coverage of monitoring sties in the middle part of the country and in the West. The data does not allow for a comprehensive picture of the mercury problem in North America.